

RUBBER MIXTURES FOR ROLL COVERINGS

5 FIELD OF THE INVENTION

This invention relates to a rubber mixture containing a carboxylated nitrile rubber, a metal salt of an acrylate, a liquid acrylate, a silane, optionally together with further additives, to a process for the production thereof and to use for moldings of all kinds, in particular roll coverings.

10 BACKGROUND OF THE INVENTION

Rolls with a covering of rubber are used in many applications, inter alia in the printing and textiles industry, in machinery, such as fax machines, and in the steel and papermaking industries.

Prior application DE-A-199 42 743 discloses a rubber mixture  
15 containing a nitrile rubber, a metal salt of an acrylate, a liquid acrylate, a silane, optionally together with further additives, to a process for the production thereof and use for moldings of all kinds, in particular roll coverings. A carboxylated nitrile rubber is, however, not disclosed.

Especially in the steel and papermaking industries, roll coverings  
20 are exposed to extreme stresses. In such applications, the coverings are primarily required to exhibit a combination of the following properties:

- low compression set
- low abrasion
- slight swelling in the media used
- 25 - good thermal and chemical resistance
- excellent adhesion between the covering and metal substrate
- slight heat build-up on exposure to stress.

SUMMARY OF THE INVENTION

We have now found that a rubber mixture containing a nitrile  
30 rubber, which furthermore, contains a metal salt of an acrylate, a liquid acrylate and a silane, is particularly suitable as a starting material for rubber coverings for rolls.

"Express Mail" mailing label number ET700175880US

Date of Deposit January 15, 2002

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The present invention accordingly provides a rubber mixture containing

- a) one or more carboxylated nitrile rubbers
- b) one or more metal salts of an acrylate
- 5 c) one or more liquid acrylates optionally applied onto a support,
- d) from 0.01 to 10 phr of one or more silanes, and
- c) optionally further additives and/or fillers.

#### DETAILED DESCRIPTION OF THE INVENTION

Nitrile rubbers are taken to mean diene/(meth)acrylonitrile  
10 copolymers. Preferred dienes in this connection are isoprene and in particular, butadiene. The copolymers have a content of copolymerized acrylonitrile and/or methacrylonitrile units of 5 to 60, preferably of 10 to 50 wt. %.

Hydrogenated nitrile rubbers are furthermore, explicitly subsumed  
15 within this term. For the purposes of this invention, "hydrogenated nitrile rubber" or "HNBR" should be taken to mean nitrile rubbers, the C=C double bonds of which have been partially or entirely hydrogenated in a selective manner (i.e. without hydrogenation of the C≡N triple bond). Preferred hydrogenated nitrile rubbers are those having a degree of  
20 hydrogenation, relative to the C=C double bonds originating from the butadiene, of at least 75, preferably of at least 95, in particular of at least 98%. The degree of hydrogenation may be determined by NMR and IR spectroscopy.

Carboxylated nitrile rubbers are taken to mean nitrile rubbers which  
25 bear acid (-COOH) or ester (-COOR) side groups. The production of such carboxylated nitrile rubbers is described, for example, in EP-A1-0 933 381 or U.S. Patent No. 5,157,083. The carboxylated nitrile rubber described in CA-2,304,501 is, however, particularly suitable.

The hydrogenation of nitrile rubber is known; U.S. Patent No.  
30 3,700,637, DE-A-2 539 132, DE-A-3 046 008, DE-A-3 046 251, DE-A-3 227 650, DE-A-3 329 974, EP-A-111 412, and FR-B-2 540 503.

Hydrogenated nitrile rubber is distinguished by elevated tear strength, slight abrasion, low residual deformation after exposure to compressive or tensile stresses and good oil resistance, but above all by remarkable stability on exposure to thermal and oxidative stresses. Hydrogenated  
5 carboxylated nitrile rubbers are accordingly preferred for the purposes of the present invention. The hydrogenated, carboxylated nitrile rubber described in CA-2,304,501 is very suitable.

Preferred mixtures are those in which the carboxylated nitrile rubber is selected from carboxylated NBR, partially hydrogenated carboxylated  
10 NBR and completely hydrogenated carboxylated NBR or mixtures of two or more of the members of the group.

Suitable nitrile rubbers generally have Mooney viscosities (DIN 53 523, ML 1+4) of 25 to 100 MU, preferably 40 to 80 MU.

It is known to add metal salts of an acrylate to mixtures containing  
15 nitrile rubbers. Suitable acrylates may be in unsubstituted or substituted form. Examples of substituted acrylates are methacrylates.

Suitable acrylates are known to the person skilled in the art from EP-A1-0 319 320, in particular page 3, lines 16 to 35, from U.S. Patent No. 5,208,294, in particular column 2, lines 25 to 40, from U.S. Patent No.  
20 4,983,678, in particular column 2, lines 45 to 62. Zinc acrylate, zinc diacrylate and zinc dimethacrylate may, in particular, be mentioned in this connection.

It may be advantageous to add the metal salt of the acrylate together with a scorch retarder. Compounds which may be considered for  
25 this purpose are, for example, hindered phenols, such as methyl-substituted aminoalkylphenols, in particular 2,6-di-tert.-butyl-4-dimethylaminomethylphenol.

Any acrylate known to the person skilled in the art which is liquid at room temperature may be considered as the liquid acrylate.

30 Trimethylolpropane trimethacrylate (TRIM), butanediol dimethacrylate (BDMA) and ethylene glycol dimethacrylate (EDMA) are preferred.

In order to achieve better incorporability, it may be advantageous to use the liquid acrylate bound on a support. Supports which may be considered are, for example, silicates, precipitated silicas, clays, carbon black, talcum or polymers. Mixtures containing 5 to 50 wt.% of support are generally used.

Silanes can be used as reinforcing additives. Vinylsilanes, such as vinyltrimethoxysiloxane or vinyltris(2-methoxyethoxy)silane, are used for peroxide vulcanization. These silanes are commercially available.

The silanes are used in quantities ranging from 0.01 to 10 phr, preferably in the range from 1 to 3 phr.

The unit "phr" is taken to mean parts by weight per 100 parts by weight of rubber.

Mixtures of various silanes may also be used.

It may also be advantageous to use the entire quantity of silane or also a proportion in a form applied onto a support.

Suitable supports are any fillers disclosed in the present invention, which may optionally be pretreated.

Further additives, which may be considered are, for example, vulcanization activators known to the person skilled in the art, in particular metal oxides, such as zinc oxide or magnesium oxide, antioxidants, such as alkyl-substituted diphenylamines, mercaptobenzimidazoles, unsaturated ethers, such as Vulkazon® AFD (Bayer AG, DE) or cyclic, unsaturated acetals, such as Vulkazon® AFS/LG (Bayer AG, DE). Further additives which may be mentioned are:

- plasticizers, in particular carboxylic acid esters, such as sebacic acid and the derivatives thereof or trimellitic acid and the derivatives thereof
- processing auxiliaries, in particular stearic acid the derivatives thereof, such as zinc stearate or polymers, such as polyethylene/vinyl acetate (Levapren® from Bayer AG, DE) or polyethylene/vinyl acrylate (VAMAC® from DuPont).

It may, furthermore, be advantageous to incorporate fillers into the rubber mixture according to the present invention. These fillers may or may not have a reinforcing action.

Fillers which may be mentioned, by way of example, are:

- 5     -     carbon blacks, such as MT, GPF, SRF and, especially, FEF, carbon blacks,
- metal oxides, such as titanium dioxide (especially as a white pigment)
- silicates, such as sodium aluminum silicate
- 10    -     silicas, in particular precipitated silicas

Improved abrasion is suitably achieved by preferably using so-called active fillers according to proposal ISO 5794, appendix D, part 1, for example published on page 535 of Handbuch für die Gummiindustrie, published by Bayer AG, 1992, Leverkusen.

- 15    -     clays, mica, talcum.

Pigments may, furthermore, be added.

The quantities of the individual components in the mixture are a function of the intended purpose of the mixture and may be determined by some preliminary testing.

- 20         The substances are generally used in the following quantities (in each case in phr = parts per hundred parts of rubber):

- metal salt of an acrylate 10 to 120 phr, preferably 10 to 85 phr, more preferably 20 to 65 phr,
- liquid acrylate 5 to 80 phr, preferably 20 to 60 phr, in each case
- 25         calculated without support,
- antioxidant 0 to 4 phr,
- retarder 0 to 2 phr,
- metal oxides, such as ZnO, 0 to 30 phr,
- fillers 0 to 150 phr, preferably active fillers,
- 30         -     silanes 0 to 10 phr,
- plasticizers 0 to 20 phr,
- processing auxiliaries 0 to 2 phr.

The present invention also provides vulcanizable mixtures containing the rubber mixtures according to the present invention, as well as a process for the production of the rubber mixtures according to the present invention and vulcanizable rubber mixtures, characterized in that the components are mixed in a mixing unit.

The mixtures are advantageously produced in a laboratory kneader (for example GK 1.5 E from Krupp Elastomertechnik, Hamburg), cooling water temperature in the range from 10 to 50°C, rotary speed of paddle in the range from 5 to 70 rpm, piston pressure 6 bar, filling level of kneader 50 to 95%, relative to the kneader chamber volume.

The following mixing sequence is advantageous: initially introduce the rubber, add remaining constituents after 0.5 to 5 minutes' running, empty the kneader at a batch temperature of <130°C. The peroxide is preferably subsequently incorporated on a roll mill (Krupp Elastomertechnik, Hamburg), roll diameter 200 mm, working width 350 mm) at a cooling water temperature of 10 to 50°C.

Vulcanizable mixtures are produced from the mixtures according to the present invention by adding vulcanizing agents to the rubber mixtures according to the present invention. Suitable vulcanizing agents are peroxide systems and combinations of peroxide systems and zinc peroxide (supported or polymer-bound, active substance content 30 to 50%).

Preferred peroxide systems comprise

- dialkyl peroxides,
- ketal peroxides,
- aralkyl peroxides,
- peroxide ethers,
- peroxide esters, such as for example
- di-tert.-butyl peroxide
- bis(tert.-butylperoxyisopropyl)benzene,
- dicumyl peroxide,

2,5-dimethyl-2,5-di-(tert.-butylperoxy)hexane,  
2,5-dimethyl-2,5-di-(tert.-butylperoxy)-3-hexene,  
1,1-bis(tert.-butylperoxy)-3,3,5-trimethylcyclohexane,  
benzoyl peroxide,

- 5 tert.-butylcumyl peroxide and  
tert.-butyl perbenzoate.

The quantities of peroxide are in the range from 1 to 10 phr,  
preferably in the range from 4 to 8 phr, relative to rubber. The quantities of  
zinc peroxide are in the range from 1 to 10 phr, preferably in the range  
10 from 4 to 8 phr, relative to rubber. Combinations of peroxide and zinc  
peroxide generally yield a higher level of vulcanization and hardness.  
Vulcanization may proceed at temperatures of 100 to 200°C, preferably of  
130 to 180°C, optionally under a pressure of 10 to 200 bar. After  
vulcanization, the vulcanizates may be conditioned by being kept at  
15 elevated temperature.

The peroxides may advantageously also be used in polymer-bound  
form. Such systems are commercially available, such as for example  
Polydispersion T(VC) D-40 P from Rhein Chemie Rheinau GmbH, DE (=  
polymer-bound di-tert.-butylperoxyisopropylbenzene).

- 20 Vulcanization may also be achieved by high-energy radiation.

For the purposes of the present invention, vulcanization means that  
less than 10, preferably less than 5 wt.%, relative to rubber, is extractable  
by 10 hours' extraction in a Soxhlet apparatus with toluene as the  
extracting agent.

- 25 The optimum quantity of vulcanizing agent is readily determined by  
preliminary testing. It is known in this connection that the required quantity  
of peroxide is indirectly proportional to the residual double bond content of  
the rubber.

- 30 The mixing unit used may be any mixing unit for rubbers known to  
the person skilled in the art, in particular kneaders and roll mills.

Care must be taken in this connection that the rubber is not degraded during the mixing operation. It may be advantageous to provide cooling during the mixing operation. In order to avoid scorching, the peroxide and zinc peroxide are frequently added as the final component, optionally in a separate mixing operation.

The present invention also provides for the use of the rubber mixtures according to the present invention for the production of moldings of any kind, preferably, coverings for rolls, more preferably, rolls for the papermaking, textiles, printing and steel industry.

Rolls generally contain a metal core of variable diameter. The metal core generally contains steel of variable composition, onto which the vulcanizable rubber mixture is applied using processes conventional in the prior art and then vulcanized. Good adhesion between the covering and metal and within the covering is essential in this connection. It may be advantageous to improve adhesion between the covering and metal by means of coupling agents such as dispersions/solutions of halogenated polymers, optionally with crosslinking agents/fillers/pigments. These substances are commercially available.

The rubber mixtures according to the present invention are suitable for roll applications because, once vulcanized, they combine excellent hardness and excellent mechanical properties in the range from above 20 Shore D to DIN 53 506, even at elevated service temperatures, with good resistance to abrasion, heat, water and basic chemicals. This balanced range of properties cannot be achieved according to the prior art. The rubber mixtures according to the present invention are, of course, also suitable for the production of other moldings, such as profiles, belts, rings, seals, damping elements etc.

For this reason, the present invention also provides moldings, in particular rolls and belts, which may be produced using a rubber mixture according to the present invention.



It is also possible to fine tune the properties of the mixtures according to the invention by adding further polymers, such as BR, NR, IIR, IR, EPDM, EPM, CR, SBR, AEM, ACM or fluoropolymers.

5 The following Examples are intended to illustrate the invention without limiting it.

### EXAMPLES

#### Measurement methods

	Residual double bond content	IR spectroscopy
	Mooney viscosity	ASTM D 1646 (stated in MU)
10	(ML 1+4 (100°C))	
	Volatile constituents (wt.%)	ASTM D 1416
	Ash content (wt.%)	ASTM D 1416
	Acrylonitrile (ACN) content	in accordance with method below:
	(wt.% bound in polymer)	

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#### Brief description of method for determining ACN

The rubber is analyzed by being pyrolyzed in a stream of oxygen on a catalyst at 900°C. The unconsumed oxygen is absorbed in a copper reduction reactor and the resultant NO-X gases are reduced to nitrogen.

20 The CO<sub>2</sub> is then removed from the stream of gas under analysis in an Na<sub>2</sub>CO<sub>3</sub>/NaOH trap, while any water is removed in an MgClO<sub>4</sub> trap. The change in thermal conductivity of the gas under analysis relative to the carrier gas stream is a measure of the nitrogen content of the sample.

#### 25 Apparatus for the above method

- NA 2000 model protein analyzer, Fisons
- Micro model microbalance, Sartorius
- Evaluation unit, Digital, DECpc Lpx 433 dx with interfaces to NA 2000 and balance interface, and EAGER 200 software.

30

Chemicals & solvents for the above method

Methionine from Hekatech

Formulation constituents for the invention

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Therban® test product KA 8837	Bayer AG	20% RDB, 34% ACN, 55 MU
Therban® C 3446	Bayer AG	HNBR with 4% RDB, 34% ACN, 58 MU
Therban XT test product KA 8889	Bayer AG	HNBR with 3.5% RDB, 32% ACN, 74 MU, carboxylic acid 5%
Zinkoxyd aktiv	Bayer AG	Active zinc oxide
Magnesium oxide paste	Treffert Rheinau GmbH	Magnesium oxide paste
Rhenofit DDA-70	Rhein Chemie Rheinau GmbH	Diphenylamine derivative
Vulkanox® ZMB 2	Bayer AG	Zinc methylmercapto- benzimidazole
Tronox® R-UF	McGee	Titanium dioxide, rutile type
Vulkasil® S	Bayer AG	Precipitated silica
Sartomer SR633	Sartomer	Zinc diacrylate with added retarder
Sartomer SR634	Sartomer	Zinc dimethacrylate with added retarder
Rhenofit® TRIM/S	Rhein Chemie Rheinau GmbH	Trimethylolpropane trimethacrylate 70%/bound to silica 30%
Ethanox 703	Albemarle, BE	2,6-di-tert.-butyl-4-(dimethyl- amino)phenol
Polydispersion T(VC) D-40 P	Rhein Chemie Rheinau GmbH	Di-(tert.-butylperoxyisopropyl)- benzene, polymer-bound
Zinc peroxide 55%	Riedel de Haan	Zinc peroxide (on filler)
Silquest RC-1 (silane)	UCC	Vinylsilane
Armeen 18 D	Flexys	Octadecylamine

Production of the mixtures

- The mixtures were produced in a GK 1.5 E laboratory kneader (Krupp Elastomertechnik, Hamburg), cooling water temperature 50°C, rotational speed of paddle 50 rpm, piston pressure 6 bar, filling level of kneader 70-80%, relative to the kneader chamber volume.
- Mixing sequence: Initially introduce rubber, add remaining constituents after 1 minute's running, empty the kneader at a temperature of <130°C.

The peroxide was subsequently incorporated on a roll mill (Krupp Elastomertechnik, roll diameter 200 mm, working width 350 mm) at a cooling water temperature of 40°C.

- The sheets for determining mechanical properties were
- 5 crosslinked/vulcanized under the stated conditions in a vulcanizing press (Krupp Elastomertechnik) between Teflon films.

#### Testing of the mixtures

<u>Value:</u>		<u>Properties:</u>	<u>Test standard:</u>
	<u>Dimension</u>		
ML 1+4, 100°C	MU	Mooney viscosity	DIN 53523, part 3
MS-T5, 120°C	min	Mooney scorch behaviour (time to 5 MU above minimum)	DIN 53523, part 4
<u>MDR rheometer</u>		Vulcanization profile	DIN 53529, part 3
Minimum, maximum, Max.-Min.	<u>S'dNm</u>	Minimum/maximum torque, max./min. difference	
T10, T50, T80, T90	min	Time to 10%, 50%, 80%, 90% conversion	
F	MPa	Tensile strength	DIN 53504
D	%	Elongation at break	DIN 53504
S xxx	MPa	Modulus at xxx% elongation	DIN 53504
H	Shore A/D	Hardness	DIN 53505
E	%	Rebound elasticity	DIN 53512

#### 10 Example 1

Mixtures 1a to 1e were produced as described in the "production of the mixtures" section from the starting materials described in Table 1 and were tested.

The test results are shown in Table 2.

Table 1

Mixture	Mixture 1a	Mixture 1b	Mixture 1c	Mixture 1d	Mixture 1e
Therban C3446(a)	100	75	50	-	-
Therban XT KA8889	-	25	50	100	100
Vulkasil S	30	30	30	30	30
Vinylsilane (Silquest RC-1)	2	2	2	2	2
Tronox R-UF	3	3	3	3	3
Rhenofit DDA-70	1.3	1.3	1.3	1.3	1.3
Vulkanox ZMB-2	0.5	0.5	0.5	0.5	0.5
Rhenofit TRIM/S	15	15	15	15	15
Sartomer SR 633	15	15	15	15	-
Sartomer SR 634	-	-	-	-	15
Ethanox 703	1	1	1	1	1
Zinc peroxide	6	6	6	6	6
Polydispersion T (VC) D-40 P	6	6	6	6	6
Armeen 18 D	3	3	3	3	3
Total parts by weight	179.8	179.8	179.8	179.8	179.8
Density (g/cm <sup>3</sup> )	1.19	1.20	1.20	1.21	1.20

Table 2

Mixture properties	Mixture 1a	Mixture 1b	Mixture 1c	Mixture 1d	Mixture 1e
MS-T5/120°C	>45	>45	>45	>45	>45
MDR rheometer 160°C/run time 40 min					
Minimum (S'dNm)	1.3	1.3	1.5	1.9	1.8
Maximum	65.7	74.8	73.8	52.9	55.8
Max.-Min.	64.4	73.5	72.2	51.0	54.1
T10 (min)	3.1	3.2	3.1	3.6	3.7
T50	6.6	6.4	6.0	6.4	7.4
T80	15.2	14.3	13.0	12.7	17.0
T90	21.7	20.6	19.1	18.5	24.2
MDR rheometer 180°C/run time 10 min					
Minimum (S'dNm)	1.0	1.0	1.2	1.4	1.3
Maximum	61.7	69.9	62.6	41.3	35.3
Max.-Min.	60.7	68.9	61.4	39.9	33.9
T10 (min)	0.7	0.7	0.7	0.7	0.8
T50	1.1	1.0	1.0	1.0	1.6
T80	2.4	2.2	2.0	1.9	3.5
T90	3.4	3.2	3.0	2.9	5.0
Vulcanization 30 min 160°C					
F (MPa)	23.4	25.5	25.3	36.2	35.6
D (%)	325	285	205	245	270
S 50 (MPa)	4.5	8.3	10.8	9.1	9.2
S 100 (MPa)	7.3	12.3	16.5	17.3	16.2
H 23°C (Sh. A)	90	94	93	92	92
H 23°C (Sh. D)	39	48	49	46	49
E 23°C (%)	45	44	40	34	34
Tear propagation resistance to DIN 53515 (N/mm)	25	29	27	21	28

Example 2

Mixtures 2a to 2e were produced in a similar manner to Example 1 from the starting materials described in Table 3 and were tested.

The results are shown in Table 4.

5

Table 3

Mixture	Mixture 2a	Mixture 2b	Mixture 2c	Mixture 2d	Mixture 2e
Therban KA 8837	100	100	-	-	50
Therban XT KA8889	-	-	100	100	50
Zinkoxyd Aktiv	2	2	-	-	-
MgO paste	2	2	-	-	-
Vulkasil S	50	50	50	50	50
Vinylsilane (Silquest RC-1)	2	2	2	2	2
Tronox R-UF	3	3	3	3	3
Rhenofit DDA-70	1.3	1.3	1.3	1.3	1.3
Vulkanox ZMB-2	0.5	0.5	0.5	0.5	0.5
Rhenofit TRIM/S	30	30	30	30	30
Sartomer SR 633	30	-	30	-	30
Sartomer SR 634	-	30	-	30	-
Ethanox 703	1	1	1	1	1
Zinc peroxide	-	-	6	6	6
Polydispersion T (VC) D-40 P	6	6	6	6	6
Armeen 18 D	3	3	3	3	3
Total parts by weight	230.8	227.8	229.8	229.8	229.8
Density (g/cm <sup>3</sup> )	1.27	1.27	1.29	1.29	1.29

Table 4

Mixture properties	Mixture 1a	Mixture 1b	Mixture 1c	Mixture 1d	Mixture 1e
MS-T5/120°C	>45	>45	>45	>45	>45
MDR rheometer 160°C/run time 40 min					
Minimum (S'dNm)	1.6	1.5	1.4	1.5	1.5
Maximum	233.4	177.0	206.4	177.2	224.5
Max.-Min.	231.7	175.5	205.0	175.7	223.0
T10 (min)	3.0	3.6	3.7	4.2	3.5
T50	4.3	6.0	5.9	6.2	4.4
T80	7.8	13.8	10.5	11.9	6.3
T90	10.2	19.7	14.3	16.9	7.9
MDR rheometer 180°C/run time 10 min					
Minimum (S'dNm)	1.3	1.3	1.0	1.2	1.2
Maximum	232.9	176.2	170.1	139.6	229.4
Max.-Min.	231.5	174.9	169.1	138.5	228.2
T10 (min)	0.6	0.7	0.7	0.9	0.7
T50	0.7	1.1	0.8	1.3	0.8
T80	0.9	2.5	1.3	2.6	0.9
T90	1.0	3.7	2.0	3.6	0.9
Vulcanization 30 min 160°C					
F (MPa)	16.2	16.7	24.8	29.7	25.1
D (%)	63	94	48	69	33
S 20 (MPa)	11.2	9.7	18.5	21.6	24.0
S 50 (MPa)	14.2	12.7	25.7	27.6	-
S 100 (MPa)	-	-	-	-	-
H 23°C (Sh. A)	98	99	99	99	99
H 23°C (Sh. D)	64	60	68	68	70
E 23°C (%)	53	45	44	43	52
Tear propagation resistance to DIN 53515 (N/mm)	35	33	28	35	37

The rubber mixtures listed in the Examples exhibit the advantageous properties stated above.

Further improvement in mechanical properties (in particular tensile strength) and hardness is achieved by blending carboxylated hydrogenated nitrile rubber with hydrogenated/partially hydrogenated nitrile rubber or by using this carboxylated hydrogenated nitrile rubber alone, which makes these rubber mixtures particularly suitable for the stated applications.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

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